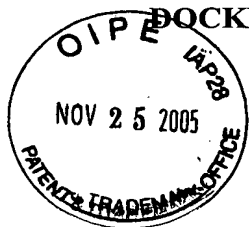


IFW



DOCKET NO.: CARP-0107

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In Re Application of:

Andrea Marsella et al.

Confirmation No.: 7472

Application No.: 10/630,551

Group Art Unit: 1754

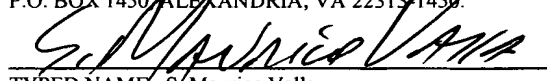
Filed: July 29, 2003

Examiner: Cam N. Nguyen

For: A HOLLOW PELLET SUITABLE AS CARRIER OF CATALYSTS FOR
SELECTIVE EXOTHERMIC REACTIONS

DATE OF DEPOSIT: November 22, 2005

I HEREBY CERTIFY THAT THIS PAPER IS BEING
DEPOSITED WITH THE UNITED STATES POSTAL
SERVICE AS FIRST CLASS MAIL, POSTAGE PREPAID,
ON THE DATE INDICATED ABOVE AND IS
ADDRESSED TO THE COMMISSIONER FOR PATENTS,
P.O. BOX 1450, ALEXANDRIA, VA 22313-1450.


TYPED NAME: S. Maurice Valla
REGISTRATION NO.: 43,966

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

**TRANSMITTAL OF CERTIFIED COPY OF PRIORITY APPLICATION
PURSUANT TO 37 CFR § 1.55**

Attached please find the certified copy/copies of the foreign application from which
priority is claimed for this case:

Country:	Application No.:	Filing Date:
European	02255354.9	July 31, 2002


- ☒ The fee of \$130.00 for entry of late priority documents is enclosed herewith. Please charge any deficiency or credit any overpayment to Deposit Account No. 23-3050.
- ☒ The Commissioner is hereby authorized to charge payment of the above fees associated with this communication or credit any overpayment to Deposit Account No. 23-3050. This sheet is attached in duplicate.

THIS PAGE BLANK (USPTO)

DOCKET NO.: CARP-0107

Date: November 22, 2005

Woodcock Washburn LLP
One Liberty Place - 46th Floor
Philadelphia PA 19103
Telephone: (215) 568-3100
Facsimile: (215) 568-3439


PATENT
S. Maurice Valla
Registration No. 43,966

© 2005 WW

THIS PAGE BLANK (USPTO)



**Europäisches
Patentamt**

**European
Patent Office**

**Office européen
des brevets**

Bescheinigung

Certificate

Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

02255354.9

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

THIS PAGE BLANK (USPTO)



Anmeldung Nr:
Application no.: 02255354.9
Demande no:

Anmeldetag:
Date of filing: 31.07.02
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

EVC TECHNOLOGY AG
Baarerstrasse 2
6300 Zug
SUISSE

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se référer à la description.)

A hollow pellet suitable as carrier of catalysts for selective exothermic reactions

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s)
revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

B01J32/00

Am Anmeldetag benannte Vertragsstaaten/Contracting states designated at date of
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR IE IT LI LU MC NL PT SE SK TR

THIS PAGE BLANK (USPTO)

A hollow pellet suitable as carrier of catalysts for selective exothermic reactions

This invention relates to novel catalyst pellets for exothermic reactions in
5 tube reactors using a fixed bed catalyst.

The exothermic reactions are not particularly limited. Preferably the catalyst pellets are used for selective chlorination and/or oxychlorination of alkenes or alkanes and selective oxidation of alkenes. For sake of clarity, the present invention is described particularly with reference to catalyst pellets for the
10 oxychlorination of ethylene to 1,2-dichloroethane.

The vapour-phase oxychlorination of ethylene to 1,2-dichloroethane using a fixed bed reactor containing a supported catalyst, usually a supported copper catalyst, is widely used commercially, for example as a part of the process for producing vinyl chloride monomer. The industry is constantly seeking to improve
15 the efficiency of the process, and much work has been reported on the effects of different catalysts on the process. Thus, both the composition and physical presentation of the catalyst have been studied. The present invention is concerned in particular with the physical shape of the catalyst.

Over the last few years some improvements have been reported in catalytic
20 performance obtained by suitable modification of the shape and/or size of catalysts in pellet form. Such characteristics affect some of the most important properties of the catalytic bed in fixed bed reactors, such as: i) the resistance to the reactant flux (pressure drop), which determines the maximum possible flow through the reactor; ii) the efficiency of heat exchange, which allows the removal
25 of heat from the highly exothermic oxychlorination reaction; and iii) the effectiveness of the pellet as far as the diffusion of reactants and reaction products inside the pellets is concerned.

A low pressure drop favours the flow through the catalytic bed, and therefore allows the increase of the productivity of industrial reactors. On the other
30 hand the increase of the pressure drop with the catalyst lifetime is a common reason for replacing the catalyst in industrial reactors, an initial low pressure drop allows a larger range of pressure drop increase and, consequently, a longer use of the catalyst before its replacing.

Starting from the usual catalysts, shaped as spheres or solid cylinders, a lower pressure drop through the catalytic bed has been obtained by developing catalysts based on hollow pellets shaped with a columnar configuration and a circular or multilobed cross-section, which give rise to catalytic beds with higher
5 void fractions and, consequently, with lower pressure drop.

Catalysts of this type, for use in oxychlorination reactions, have been described for example in the following patents or patent applications.

USP 4366093 reports a hollowed cylindrical catalyst having an outer diameter D_e in the range 3-6 mm, an internal diameter $D_i \geq 1$ mm, a wall thickness
10 of at most 1,5 mm and a length L in the range 3-6 mm.

USP 4382021 and EP 54674 describe a hollowed cylinder catalyst having the size $D_e = 5-12$ mm, $D_i = 3-8$ mm and $L = 3-12$ mm.

USP 4740644 claims a new method for preparing hollowed catalysts and exemplifies catalysts with $D_e = 5$ mm, $D_i = 1.8$ mm and $L = 5$ mm .

15 In USP 5166120 a catalyst prepared by extrusion, shaped as a hollowed cylinder with $D_e = 4-6$ mm, $D_i = 1-2$ mm and $L = 1.7-3.75$, is described.

Hollow cylindrical pellets have a S/V (geometric surface to volume ratio) higher than spheres and solid cylinders, and this property, together with a higher void fraction of catalytic bed, gives a more efficient heat exchange. Thus, better
20 temperature control along the catalytic bed and reduced hot spot temperatures are obtained: in this way a longer catalyst life is achieved and the reaction results in a reduced formation of chlorinated by-products and combustion products.

A further benefit of hollowed cylindrical pellets, due to their higher geometric surface combined with a lower wall thickness, is their higher effectiveness,
25 because the reaction takes place only in a thin external layer. By using hollowed cylindrical pellets also the formation of carbonaceous deposits inside the core of the pellet, responsible for pellet breakage and pressure drop increase during the industrial run, is reduced; consequently, an increase of catalyst life can be obtained.

30 In order to obtain the above described advantages a hollowed pellet must be designed carefully, otherwise several disadvantages become evident. For example, if the D_i/D_e ratio of a hollowed cylinder is greater than a certain value, the pellet becomes too fragile, without further advantage in terms of effectiveness.

Moreover, the apparent bulk density of the catalyst decreases, resulting in a lower conversion per unit volume of catalyst bed due to the lower total active phase content in the reactor. This last effect can affect also the catalyst life, because the catalyst tends to lose active phase compounds in the reaction environment. A
5 solution to this problem could be an increase of the active phase concentration of fresh catalyst, because an excess of active phase compounds, even if not contributing directly to the catalyst activity, can act as a reservoir, increasing the catalyst life. However the active phase concentration can not be increased over a certain extent, because the consequent loss of the catalyst surface area causes a
10 loss of activity.

A further improvement for pellets having a hollowed cylinder shape is described in the patent application EP 1053789 in the name of the Applicant, wherein a particular hollow cylinder size of the pellet is described.

Catalyst having a shape different from a hollowed cylinder have been also
15 investigated. WO 96/40431 describes a catalyst for ethylene oxychlorination having a partially hollow cylindrical shape with internal reinforcing vanes. The cross-section is shaped like a "spoked wheel", the outer diameter D_e is greater than 6.5 mm, the wall thickness is in the range of 0.1 to 0.3 times D_e and the length is in the range of 0.5 to 5 times D_e .

20 EP 687331 discloses an ethylene oxychlorination catalyst in granular form, consisting of copper chloride supported on an alumina carrier, having a columnar configuration with a trilobed cross-section provided with three through-bores coaxial with said lobes. The axes of the lobes are substantially parallel to each other and substantially equidistant from each other.

25 With these particular configurations of said patents, more complex than the hollowed cylinder, it was tried to improve one or more of the relevant features described above, i.e.: i) reduction of the pressure drop, ii) increase of the S/V factor, iii) reduction of the pellet wall thickness. However these configurations show low bulk density and/or low mechanical resistance, which can reduce or,
30 even, overcome the achieved improvements in terms of reactor productivity and catalysts lifetime.

The above remarks make clear that, producing pellet shaped oxychlorination catalysts, it must be taken into account that every change capable

of giving rise to some improvement in catalytic performance can also cause unwanted detrimental effects, especially if the changes are not balanced carefully by the simultaneous modification of other characteristics. As a conclusion, in order to obtain an excellent oxychlorination catalyst it is not sufficient to optimise a single
5 characteristic: all the properties must be carefully balanced as a whole. It was felt the need to have available catalyst pellets which show a good combination of the above described requirements without the disadvantages reported above: i) lower pressure drop of the catalytic bed due to the particular shape of the pellet which increases the void fraction of the catalytic bed, ii) better heat exchange, iii) good
10 effectiveness, iv) good mechanical resistance of the pellets in order to have pellets not too fragile, v) high bulk density guaranteeing a high total active phase content of the reactor. A good combination of the above features would allow to obtain in the oxychlorination reaction the following advantages: i) improved selectivity, ii) good conversion, iii) longer catalyst lifetime.

15 An object of the present invention is therefore a catalyst pellet for selective gas phase exothermic reactions in a tubular fixed bed reactor, wherein said catalyst pellet has:

- I. an uniform cross-section or, if not uniform, with a deviation from the average cross-section area lower than 30%;
- 20 II. a parallelogram cross-section, preferably a rhomboidal or square cross-section;
- III. one or more through-bores:
 - A. with axes which are parallel to each other and to the axis of the pellet or, if not parallel, with a deviation from parallel line lower than 20%;
 - 25 B. with uniform section or, if not uniform, with a deviation from the average cross-section lower than 30%, particularly with one of the following embodiments:
 1. with one bore having the same shape of the cross-section of the pellet or, optionally, with two or more bores obtained by introducing internal
30 reinforcing vanes in said one bore;
 2. with two or more bores having a rounded shape, particularly a circular or elliptical shape and, if four or more bores are present, with different distances between the centres of the non-adjacent couples of bores.

Some very schematic examples are reported in Figure 1 to illustrate, but not to limit, the present invention. The Figure shows three possible embodiments based on the same external rhomboidal cross-section and with four bores. In example A the four bores have been obtained from one bore having the same shape of the external contour of the pellet cross introducing two reinforcing vanes connecting the edges of the rhomb. In example B the four bores have been obtained from one bore having the same shape of the cross-section of the pellet introducing two reinforcing vanes connecting the sides of the rhomb. In example A the four bores are elliptical.

10 The sides of the external cross-section of the pellet may also be curved and its corners may be rounded in order to confer an improved mechanical strength, to reduce the abrasion and to favour the manufacture. The ratio between the area of the cross-section of the pellet, including the cross-section of the bores, and the area of the parallelogram circumscribing the external contour of the pellet cross-section is higher than 0.75, preferably higher than 0.85. The curves may be convex or concave or both. The whole external contour of the pellet cross section may be convex or the curves corresponding to the sides of the external contour of the pellet cross-section may be concave and the curves corresponding to the edges of the external contour of the pellet cross-section may be convex. In the embodiment containing bores with circular or elliptical cross-section, the convex curve corresponding to the edges and the concave curve corresponding to the sides of the cross-section are preferred.

25 The pellets with one bore having the same shape of the cross-section of the pellet or, optionally, with two or more bores obtained by introducing internal reinforcing vanes in said one bore may have the sides and/or the corners of the contour of the bores cross-section rounded in such a way that the ratio between the area of the cross-section of the bores and the area of the parallelogram circumscribing the external contour of the bores cross-section is higher than 0.75, preferably higher than 0.85. The reinforcing vanes of the pellets having one bore with the same shape of the external contour of the pellet cross-section preferably are disposed to connect the opposite edges or the opposite sides of the external contour of the bore cross-section.

When more than one bore is present in the pellet, they can have the same size or different size, preferably the bores have the same size.

The catalyst pellets of the present invention have the following size: $4\text{ mm} < P_1 < 15\text{ mm}$, $4\text{ mm} < P_2 < 15\text{ mm}$, $0.5\text{ mm} < P_3 < 4\text{ mm}$, $3\text{ mm} < P_4 < 15\text{ mm}$,
 5 wherein P_1 is the main diagonal of the parallelogram, P_2 is the secondary diagonal of the parallelogram, P_3 is the maximum wall thickness, P_4 is the length of the parallelogram. It is meant for wall thickness the minimum distance between a given point of the bore wall and the external wall of the pellet or the wall of an adjacent bore. When the bores have circular shape the diameter is in the range of
 10 0.7 to 3 mm.

The catalyst pellets of the present invention have preferably the following size: $4\text{ mm} < P_1 < 9\text{ mm}$, $4\text{ mm} < P_2 < 9\text{ mm}$, $0.7\text{ mm} < P_3 < 2\text{ mm}$, $4\text{ mm} < P_4 < 8\text{ mm}$, wherein P_1 , P_2 , P_3 and P_4 have the meaning above indicated.

Some examples are shown in Figures 2-4, which represent preferred
 15 embodiments of the invention. In Figure 2 a pellet having a rhomboidal cross-section with one reinforcing vane and two bores is reported. In Figure 3 a pellet having a square cross-section with two reinforcing vanes and four bores is reported. Alternatively to the square cross-section of Figure 3 a pellet with a rectangular cross-section is suitable for use. In Figure 4 a pellet having a
 20 rhomboidal cross-section with four circular bores is reported.

With reference to Figure 2, the catalyst pellet of the present invention has the following size: $4\text{ mm} < R_1 < 15\text{ mm}$, $4\text{ mm} < R_2 < 15\text{ mm}$, $0.5\text{ mm} < R_3 < 3\text{ mm}$, $3\text{ mm} < R_4 < 15\text{ mm}$, wherein R_1 is the longest size of the cross-section, R_2 is the shortest size of the cross-section, R_3 is the largest wall thickness of the bores,
 25 R_4 is the length. Preferably: $4\text{ mm} < R_1 < 9\text{ mm}$, $4\text{ mm} < R_2 < 9\text{ mm}$, $0.7\text{ mm} < R_3 < 2\text{ mm}$, $4\text{ mm} < R_4 < 8\text{ mm}$.

With reference to Figure 3, the catalyst pellet of the present invention has the following size: $3\text{ mm} < Q_1 < 10.5\text{ mm}$, $0.5\text{ mm} < Q_3 < 3\text{ mm}$, $3\text{ mm} < Q_4 < 15\text{ mm}$, wherein Q_1 is the side of the square, Q_3 is the wall thickness, Q_4 is the length.
 30 Preferably: $4\text{ mm} < Q_1 < 9\text{ mm}$, $0.7\text{ mm} < Q_3 < 2\text{ mm}$, $3\text{ mm} < Q_4 < 8\text{ mm}$.

With reference to Figure 4, the catalyst pellet of the present invention has the following size: $4\text{ mm} < T_1 < 15\text{ mm}$, $4\text{ mm} < T_2 < 15\text{ mm}$, $0.5\text{ mm} < T_3 < 3\text{ mm}$, $3\text{ mm} < T_4 < 15\text{ mm}$, wherein T_1 is the longest size of the cross-section, T_2 is the

shortest size of the cross-section, T_3 is the largest wall thickness of the bores, T_4 is the length. The diameter of the bores is comprised between 0.7 and 3 mm. Preferably: $4 \text{ mm} < T_1 < 9 \text{ mm}$, $4 \text{ mm} < T_2 < 9 \text{ mm}$, $0.7 \text{ mm} < T_3 < 2 \text{ mm}$, $3 \text{ mm} < T_4 < 8 \text{ mm}$.

5 Further examples are shown in Figures 5-7, which represent preferred embodiments of the invention with curved external surfaces. In Figure 5 the same pellet as Figure 2, but with convex external surfaces is reported. In Figure 6 the same pellet as Figure 3, but with convex external surfaces is reported. In Figure 7 the same pellet as Figure 4, but with concave external surfaces is reported.

10 The exothermic reactions in which the pellets of the present invention can be applied are not particularly limited. Preferably they are used for selective chlorination and/or oxychlorination of alkenes, e.g. ethylene, or alkanes e.g. methane and ethane; selective oxidation of alkenes, e.g. ethylene and propylene. For example it can be mentioned the reaction of ethylene with chlorine to give 1,2-
15 dichloroethane, the reaction of ethylene with hydrogen chloride and air or oxygen to give 1,2-dichloroethane, the reaction of methane with chlorine, the selective oxidation of ethylene or propylene, etc.

Preferably the catalyst pellets of the invention are used in the oxychlorination of hydrocarbons, especially the vapour phase oxychlorination of
20 ethylene to EDC. The carrier material of the catalyst of the present invention may be any of the materials known for producing supported catalysts. Examples include silica, pumice, diatomaceous earth, alumina and other aluminium hydroxo compounds such as boehmite and bayerite. For the oxychlorination reaction the preferred carrier materials are γ -alumina or other transitional aluminas and
25 boehmite, the latter normally being pre-heated to convert it into alumina. The carrier material suitably has a surface area (BET) of 50-350 m²/g. The active material supported on the carrier contains copper in an amount of 1-12 wt% based on the weight of the dry catalyst. The copper will normally be deposited on the carrier in the form of a salt, especially as halide and preferably as cupric chloride.
30 The copper may be used in combination with other metal ions in order to have the desired selectivity and conversion. Such other metals include, for example, alkali metals (such as Li, Na, K, Ru, Cs), alkaline-earth metals (such as Mg, Ca, Ba), group IIB metals (such as Zn and Cd) and lanthanides (such as La, Ce and so on)

or a suitable combination of them. These additional metal ions can be added as salts or oxides, the total amount of additives suitably being in the range 0-15 wt%. They can be added together with the copper or alternatively one or more of them (even all) after or even before the copper. In the last case their addition can be followed by an intermediate heat treatment. Preferred alkali metals are Li and K and Cs and they are preferably added as chlorides, each of them in the range 0-8 wt%. The preferred alkaline-earth metal is Mg, added in the range 0-6 wt%. Preferred lanthanides are La and Ce, each of them added in the range 0-12 wt%. The addition of the active components can be accomplished by methods well known by those of skill in catalyst preparation. Here can be mentioned, for example, dry impregnation, incipient wetness impregnation or dipping, using a suitable solution of compounds to be added, for example an aqueous solution, optionally containing also acids such as HCl. The addition of the active components can be made partially or totally before or after the formation of the hollow pellets. Preferably the catalysts are prepared by impregnation of the already formed carrier. The shaping of the carrier or the catalyst may be performed by well known methods such as tableting and extrusion. These operations are performed in the usual manner, optionally using additives such as lubricants and/or binders. Preferably the shaped pellets are obtained by tableting, in order to have a more uniform pellet size, density and higher mechanical resistance. The operations include customary thermal treatments, such as calcination of the carrier at 500-1100 K, preferably at 750-950 K, if the active part is added to the carrier after the shaping procedure and drying at 330-600 K after addition of the active components.

25 The catalytically active material for selective oxidation of alkenes contains silver. The catalytically active material may preferably also comprise at least one of alkali metals, alkaline earth metals, group IIB metals, group VIIB metals, group VIIIB metals and lanthanides in a total amount preferably up to 5 wt%. Preferably the alkali metal is cesium, the alkaline earth is barium.

30 The catalyst for the oxychlorination of alkanes contains preferably copper and/or Ni and an alkali metal for example in the atomic ratio 2:8. The alkali metal are preferably potassium or lithium or cesium. The catalytically active material may preferably also comprise at least one of alkaline earth metals, group IIB metals

and lanthanides. Preferably the alkaline earth is magnesium and the lanthanide are lanthanum or cerium.

For the selective chlorination of alkenes and alkanes, the well known active components of the catalysts are used, for example alkali metals, alkaline earth metals, group IIB metals and lanthanides in a total amount preferably up to 30 wt% of the layer.

The carriers for the above active components of the catalysts of the above reactions are preferably aluminum hydroxides, aluminum oxide-hydroxides, alumina, silica, zirconia, titania, magnesia, pumice, diatomaceous earth zeolites or their mixtures or mixed compounds. Depending on the reaction the carriers may have high or low surface area.

In addition to the exothermic reactions, the pellets of the present invention can be used also for endothermic reactions with advantages similar to those achieved in selective exothermic reactions.

The following examples refer to the oxychlorination reaction of ethylene to 1,2-diochloroethane, taken as representative of selective gas phase exothermic reactions. Such examples are given for illustrative purposes and do not limit the scope of the invention.

20

Examples

Drawings

The accompanying drawings have the purpose to illustrate, but not to limit, the invention. Figure 1 shows three possible embodiments based on the same external rhomboedrical cross-section and with four bores. In example A the four bores have been obtained from one bore having the same shape of the cross-section of the pellet introducing two reinforcing vanes connecting the edges of the rhomb. In example B the four bores have been obtained from one bore having the same shape of the cross-section of the pellet introducing two reinforcing vanes connecting the sides of the rhomb. In example A the four bores are circular.

Figure 2 is a schematic illustration, not to scale, of a catalyst pellet having a rhomboidal cross-section with one reinforcing vane and two bores.

Figure 3 is a schematic illustration, not to scale, of a catalyst pellet having a square cross-section with two reinforcing vanes and four bores.

Figure 4 is a schematic illustration, not to scale, of a catalyst pellet having a rhomboidal cross-section with four circular bores.

Figure 5 is a schematic illustration, not to scale, of a catalyst pellet having a rhomboidal cross-section with one reinforcing vane forming two bores and with
5 convex external surfaces.

Figure 6 is a schematic illustration, not to scale, of a catalyst pellet having a square cross-section with two reinforcing vanes forming four bores and with convex external surfaces.

Figure 7 is a schematic illustration, not to scale, of a catalyst pellet having a
10 rhomboidal cross-section with four circular bores and with concave external surfaces.

Experimental equipment

The choice of the method used for catalytic activity testing is very important,
15 because the differences in term of conversion and selectivity to different products exhibited by different catalysts are usually small, but of great importance in 1,2-dichloroethane production in the common industrial large scale. The only way to obtain results which are truly representative of the industrial reactor is to perform the test using a tube with the same size as an industrial one and to adopt the
20 same conditions (temperature, pressure, feed composition, flow and so on) as those used in the industrial reactor. The data reported below were obtained in a pilot plant using a tube having the same size as a typical industrial one and under a variety of different conditions covering those encountered during a typical industrial run. The reactor used (see Figure 8) was a nickel tube 8 m long with an
25 internal diameter of 27.75 mm. An external jacket with circulating steam was used to control the temperature profile. The reactor was equipped with a thermowell having an external diameter of 6 mm, containing 12 thermocouples to record the temperature profile during the tests. Two on-line gaschromatographs were used at the inlet and at the outlet of the reactor to control the reaction. The 1,2-
30 dichloroethane was collected in a vessel containing isopropyl alcohol at about 0°C and then analysed. This technique allows also the collection of the low boiling and the water soluble compounds (chloroethanol, chloral, etc.) as well as the unreacted HCl. The reactor feed was: 5200 NI/h of C₂H₄, 600 NI/h of O₂, 2.300

NI/h of HCl, 1000 NI/h of N₂. The oxygen was 6.5% vol (the flammability limit at 210°C and at 6 bar is ca. 8%). The pressure at the inlet of the reactor was 6 bar, and the temperature of the coolant was 220°C.

5 Catalysts

Seven different types of catalyst having the shape and size shown in Table 1 and the compositions shown in Table 2 were prepared on the basis of the method described above. In particular, a stearate as a lubricant was added to bohemite and the mixture was moulded into a particle having the shape and size
10 shown in Table 1, by using a tableting machine. Catalyst A was formed according to the embodiment shown in Figure 5 of the present invention (catalyst pellet having a rhomboidal cross-section with one reinforcing vane forming two bores and with convex external surfaces), catalyst B according to the embodiment shown in Figure 6 (catalyst pellet having a square cross-section with two
15 reinforcing vanes forming four bores and with convex external surfaces), catalyst C according to the embodiment shown in Figure 7 (catalyst pellet having a rhomboidal cross-section with four circular bores and with concave external surfaces). As far as the comparative examples are concerned, catalyst D is a hollow cylinder according to EP 1053789; catalyst E is a hollow cylinder according
20 to USP 4366093; catalyst F is a hollow cylinder according to USP 4740644; catalyst G is a hollow cylinder according to USP 5166120. The carrier pellets were calcined at 823 K for 5 hours, to obtain pellets made of γ -Al₂O₃ with the required surface area. The carrier was impregnated by the incipient wetness method with solutions containing a proper concentration of active compounds in order to obtain
25 two types of catalysts with the compositions set out in Table 2.

The reactor loading pattern used, the same for the different types of catalysts tested, was formed of five layers. From the top to the bottom, the layers were as follows: 1) 1200 mm long, containing type I catalyst diluted to 30 vol% with graphite (cylinders with diameter of 5 mm and length of 6.2 mm); 2) 1200 mm
30 long, containing type I catalyst diluted to 40 vol%; 3) 1200 mm long, containing type I catalyst diluted to 60 vol%; 4) 1000 mm long, containing type II catalyst diluted to 45 vol%; 5) 2400 mm long, containing type II catalyst not diluted. The overall catalytic bed was 7 m long.

A large number of tests were carried out comparing mainly the new catalysts of the present invention (A,B,C) with the old hollow cylinder catalysts (D,E,F,G) and the main results are reported in Table 3.

5 It is evident that all the catalysts of the present invention having a prism-inscribable shape (A, B, C) are superior in the performance, giving the better combination in terms of pressure drop, HCl conversion, selectivity and hot spot temperatures if compared to the hollow cylinder catalysts.

10 In particular the catalysts A and B show a lower pressure drop than the hollow cylinder ones, because the particular shape increases the void fraction of the related catalytic bed.

It is to underline that, even if the standard hollow cylinder catalyst G has a higher bed void fraction, the measured pressure drop is higher owing to the unavoidable breakage during the loading of this catalyst formed by extrusion.

15 Furthermore, taking into account that the overall amount in weight of catalyst per unit of volume of reactor tube for the new catalysts A, B, C, is lower than the standard catalysts D, E, F because of the lower bulk density due to the new shapes, we could expect a lower activity per unit volume of reactor tube and therefore a lower HCl conversion for the new catalysts. This is exactly what is
20 obtained with the standard hollow cylinder catalyst G, in comparison with the other hollow cylinder catalysts D, E, F. On the contrary, even if with the new catalysts the overall weight per unit of volume is lower, the HCl conversion is better than the one of the standard catalysts.

25 The reduced wall thickness of the new catalyst does not imply a reduced mechanical strength, because the new geometry and the well tuned tableting parameters, allow to maintain an adequate mechanical strength.

Other important results achieved with the new catalysts are the reduced by-product formation, the increase selectivity to EDC and an increased catalyst life.

Table 1

Catalyst	A	B	C	D	E	F	G
P ₁ main diagonal (mm)	7.60	5.60	5.45	-	-	-	-
P ₂ secondary diagonal (mm)	5.80	5.60	3.05	-	-	-	-
D _e external diameter (mm)	-	-	-	4.90	4.90	4.90	4.90
D _i internal diameter (mm)	-	-	-	2.25	2.25	2.00	1.30
P ₃ wall thickness (mm)	1.00	0.80	0.60	1.32	1.32	1.45	1.80
P ₄ length (mm)	6.35	6.35	6.35	6.35	5.00	5.00	9.50
Geometric volume (mm ³)	133	117	65	94	74	79	166
Geometric area (mm ²)	274	328	210	172	142	140	225
SV (mm ⁻¹)	2.06	2.80	3.21	1.82	1.91	1.78	1.35
Bed void fraction	0.60	0.64	0.59	0.57	0.55	0.53	0.64

Table 2

Catalyst		A	B	C	D	E	F	G
Type I	Carrier	γ -Al ₂ O ₃	γ -Al ₂ O ₃	γ -Al ₂ O ₃	γ -Al ₂ O ₃	γ -Al ₂ O ₃	γ -Al ₂ O ₃	γ -Al ₂ O ₃
	CuCl ₂ (%)	9.5	9.5	9.5	9.5	9.5	9.5	9.5
	KCl (%)	5.7	5.7	5.7	5.7	5.7	5.7	5.7
	Surface area (m ² /g)	127	123	125	120	124	125	124
	Bulk Density (cm ³ /g)	0.65	0.58	0.67	0.69	0.73	0.76	0.55
Type II	Carrier	γ -Al ₂ O ₃	γ -Al ₂ O ₃	γ -Al ₂ O ₃	γ -Al ₂ O ₃	γ -Al ₂ O ₃	γ -Al ₂ O ₃	γ -Al ₂ O ₃
	CuCl ₂ (%)	17.0	17.0	17.0	17.0	17.0	17.0	17.0
	KCl (%)	1.5	1.5	1.5	1.5	1.5	1.5	1.5
	Surface area (m ² /g)	148	150	155	150	155	153	152
	Bulk Density (cm ³ /g)	0.67	0.59	0.69	0.71	0.75	0.78	0.58

Table 3

Catalyst	A			B			C			D			E			F			G		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Trial	201	201	201	201	201	201	201	201	201	201	201	201	201	201	201	201	201	201	201	201	201
Inlet temp. (°C)	224	224	224	224	224	224	225	225	225	225	225	225	226	226	226	228	228	228	230	230	230
Outlet temp. (°C)	248	248	248	250	250	250	252	252	252	253	253	253	256	256	256	260	260	260	251	251	251
Hot spot temp. (°C)	220	220	220	220	220	220	220	220	220	220	220	220	220	220	220	220	220	220	220	220	220
Coolant temp. (°C)	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Inlet press. (barg)	1.7	3.5	6.4	1.2	3.4	6.3	1.5	3.7	6.2	0.8	3.0	6.8	2.0	6.3	4.6	2.9	4.4	6.1	1.5	3.5	6.5
Excess oxygen vs HCl	1.3	1.3	1.3	1.4	1.4	1.4	2.0	2.0	2.0	1.6	1.6	1.6	1.8	1.8	1.8	2.0	2.0	2.0	1.8	1.8	1.8
Pressure drop (barg)	98.9	100	100	98.8	100	100	99.2	100	100	98.4	99.9	100	98.5	99.8	100	98.4	99.1	99.6	97.9	98.4	99.5
HCl conversion (% mol)	98.5	98.8	98.9	98.4	98.7	98.8	98.3	98.6	98.8	98.3	98.6	98.7	98.2	98.4	98.5	98.0	98.2	98.4	98.2	98.5	98.6
Selectivity to EDC (% mol)	0.78	0.60	0.50	0.80	0.60	0.52	0.80	0.58	0.50	0.80	0.60	0.50	0.80	0.60	0.55	0.74	0.65	0.55	0.85	0.65	0.56
Ethyl chloride (% mol)	0.44	0.2	0.23	0.50	0.36	0.28	0.58	0.47	0.30	0.58	0.43	0.38	0.69	0.65	0.55	1.06	0.83	0.66	0.55	0.40	0.35
Chlor. by-products (% mol)	8																				
CO _x (% mol)	0.28	0.32	0.37	0.30	0.34	0.40	0.32	0.35	0.40	0.32	0.37	0.42	0.31	0.35	0.40	0.30	0.32	0.39	0.40	0.45	0.49

THIS PAGE BLANK (USPTO)

Claims

- 1 A catalyst pellet for selective gas phase exothermic reactions in a tubular fixed bed reactor, wherein said catalyst pellet has:
 - 5 I. an uniform cross-section or, if not uniform, with a deviation from the average cross-section area lower than 30%;
 - II. a parallelogram cross-section, preferably a rhomboidal or square cross-section;
 - 10 III. one or more through-bores:
 - A. with axes which are parallel to each other and to the axis of the pellet or, if not parallel, with a deviation from parallel line lower than 20%;
 - B. with uniform section or, if not uniform, with a deviation from the average cross-section lower than 30%, particularly with one of the
 - 15 following embodiments:
 - a. with one bore having the same shape of the cross-section of the pellet or, optionally, with two or more bores obtained by introducing internal reinforcing vanes in said one bore;
 - 20 b. with two or more bores having a rounded shape, particularly a circular or elliptical shape and, if four or more bores are present, with different distances between the centres of the non-adjacent couples of bores.
- 2 A catalyst pellet according to claim 1 wherein the pellet has the following
 - 25 size: $4\text{ mm} < P_1 < 15\text{ mm}$, $4\text{ mm} < P_2 < 15\text{ mm}$, $0.5\text{ mm} < P_3 < 4\text{ mm}$, $3\text{ mm} < P_4 < 15\text{ mm}$, wherein P_1 is the main diagonal of the parallelogram, P_2 is the secondary diagonal of the parallelogram, P_3 is the maximum wall thickness, P_4 is the length of the parallelogram.
- 30 3 A catalyst pellet according to claims 1 and 2 wherein the pellet has the following size: $4\text{ mm} < P_1 < 9\text{ mm}$, $4\text{ mm} < P_2 < 9\text{ mm}$, $0.7\text{ mm} < P_3 < 2\text{ mm}$, $4\text{ mm} < P_4 < 8\text{ mm}$, wherein P_1 is the main diagonal of the parallelogram, P_2 is the

secondary diagonal of the parallelogram, P_3 is the maximum wall thickness, P_4 is the length of the parallelogram.

4 A catalyst pellet according to claim 1 wherein the pellet has a rhomboidal
5 cross-section with at least one reinforcing vane connecting two opposite edges
and at least two bores.

5 A catalyst pellet according to claim 4 wherein the pellet has the following
size: $4\text{ mm} < R_1 < 15\text{ mm}$, $4\text{ mm} < R_2 < 15\text{ mm}$, $0.5\text{ mm} < R_3 < 3\text{ mm}$, $3\text{ mm} < R_4 <$
10 15 mm , wherein R_1 is the longest size of the cross-section, R_2 is the shortest size
of the cross-section, R_3 is the largest wall thickness of the bores, R_4 is the length.

6 A catalyst pellet according to claim 4 and 5 wherein the pellet has the
following size: $4\text{ mm} < R_1 < 9\text{ mm}$, $4\text{ mm} < R_2 < 9\text{ mm}$, $0.7\text{ mm} < R_3 < 2\text{ mm}$, 4
15 $\text{mm} < R_4 < 8\text{ mm}$, wherein R_1 is the longest size of the cross-section, R_2 is the
shortest size of the cross-section, R_3 is the largest wall thickness of the bores, R_4
is the length.

7 A catalyst pellet according to claim 1 wherein the pellet has a rhomboidal
20 cross-section with at least one reinforcing vane connecting two opposite sides and
at least two bores.

8 A catalyst pellet according to claim 7 wherein the pellet has the following
size: $4\text{ mm} < R_1 < 15\text{ mm}$, $4\text{ mm} < R_2 < 15\text{ mm}$, $0.5\text{ mm} < R_3 < 3\text{ mm}$, $3\text{ mm} < R_4 <$
25 15 mm , wherein R_1 is the longest size of the cross-section, R_2 is the shortest size
of the cross-section, R_3 is the largest wall thickness of the bores, R_4 is the length.

9 A catalyst pellet according to claim 7 and 8 wherein the pellet has the
following size: $4\text{ mm} < R_1 < 9\text{ mm}$, $4\text{ mm} < R_2 < 9\text{ mm}$, $0.7\text{ mm} < R_3 < 2\text{ mm}$, 4
30 $\text{mm} < R_4 < 8\text{ mm}$, wherein R_1 is the longest size of the cross-section, R_2 is the
shortest size of the cross-section, R_3 is the largest wall thickness of the bores, R_4
is the length.

10 A catalyst pellet according to claim 7 wherein the pellet has a square cross-section with at least two reinforcing vanes and four bores.

11 A catalyst pellet according to claim 10 wherein the pellet has the following
5 size: $3 \text{ mm} < Q_1 < 10.5 \text{ mm}$, $0.5 \text{ mm} < Q_3 < 3 \text{ mm}$, $3 \text{ mm} < Q_4 < 15 \text{ mm}$, wherein Q_1 is the side of the square, Q_3 is the wall thickness, Q_4 is the length.

12 A catalyst pellet according to claim 10 and 11 wherein the pellet has the following size: $4 \text{ mm} < Q_1 < 9 \text{ mm}$, $0.7 \text{ mm} < Q_3 < 2 \text{ mm}$, $3 \text{ mm} < Q_4 < 8 \text{ mm}$,
10 wherein Q_1 is the side of the square, Q_3 is the wall thickness, Q_4 is the length.

13 A catalyst pellet according to claim 1 wherein the pellet has a rhomboidal cross-section with at least four circular bores.

14 A catalyst pellet according to claim 13 wherein the pellet has the following
15 size: $4 \text{ mm} < T_1 < 15 \text{ mm}$, $4 \text{ mm} < T_2 < 15 \text{ mm}$, $0.5 \text{ mm} < T_3 < 3 \text{ mm}$, $3 \text{ mm} < T_4 < 15 \text{ mm}$, wherein T_1 is the longest size of the cross-section, T_2 is the shortest size of the cross-section, T_3 is the largest wall thickness of the bores, T_4 is the length. The diameter of the bores is comprised between 0.7 and 3 mm.

20

15 A catalyst pellet according to claim 13 and 14 wherein the pellet has the following size: $4 \text{ mm} < T_1 < 9 \text{ mm}$, $4 \text{ mm} < T_2 < 9 \text{ mm}$, $0.7 \text{ mm} < T_3 < 2 \text{ mm}$, $3 \text{ mm} < T_4 < 8 \text{ mm}$, wherein T_1 is the longest size of the cross-section, T_2 is the shortest size of the cross-section, T_3 is the largest wall thickness of the bores, T_4 is the
25 length.

16 A catalyst pellet according to claim 1 to 15 wherein the sides and/or the corners of the external contour of the pellet cross-section are rounded in such a way that the ratio between the area of the cross-section of the pellets, including
30 the cross-section of the bores, and the area of the parallelogram circumscribing the external contour of the pellet cross-section is higher than 0.75.

17 A catalyst pellet according to claim 1 to 16 wherein the sides and/or the corners of the external contour of the pellet cross-section are rounded in such a way that the ratio between the area of the cross-section of the pellets, including the cross-section of the bores, and the area of the parallelogram circumscribing the external contour of the pellet cross-section is higher than 0.85.

18 A catalyst pellet according to claim 1 to 17 wherein the sides of the external contour of the pellet cross-section are curved, the curve being convex or concave or both.

19 A catalyst pellet according to claim 1 to 18 wherein the sides of the external contour of the pellet cross-section are curved, the curve being convex.

20 A catalyst pellet according to claim 1 to 19 wherein the sides and/or the edges of the external contour of the pellet cross-section are curved, the curves corresponding to the sides of the external contour of the cross-section being concave and the curves corresponding to the edges of the external contour of the cross-section being convex.

21 A catalyst pellet according to claim 1 to 20 with one bore having the same shape of the cross-section of the pellet or, optionally, with two or more bores obtained by introducing internal reinforcing vanes in said one bore, wherein the sides and/or the corners of the contour of the bores cross-section are rounded in such a way that the ratio between the area of the cross-section of the bores and the area of the parallelogram circumscribing the external contour of the bores cross-section is higher than 0.75.

22 A catalyst pellet according to claim 1 to 21 with one bore having the same shape of the cross-section of the pellet or, optionally, with two or more bores obtained by introducing internal reinforcing vanes in said one bore, wherein the sides and/or the corners of the contour of the bores cross-section are rounded in such a way that the ratio between the area of the cross-section of the bores and

the area of the parallelogram circumscribing the external contour of the bores cross-section is higher than 0.85.

23 A catalyst pellet according to claim 1 to 22 with two or more bores obtained
5 by introducing internal reinforcing vanes in one bore having the same shape of the cross-section of the pellet, wherein said reinforcing vanes are disposed to connect the opposite edges or the opposite sides of the external contour of the bore cross-section.

10 24 Process for making the pellets according to claims 1-23, wherein the pellets are obtained by extrusion or tableting.

25 Use of the catalysts pellets according to claims 1-24 for selective gas-phase exothermic reactions.

15

26 Use of the catalyst pellets according to claim 25, wherein the gas phase exothermic reactions are the selective chlorination and/or oxychlorination of alkenes or alkanes and the selective oxidation of alkenes.

20 27 Use of the catalyst pellets according to claim 26, wherein the reactions are selected from the conversion of ethylene with chlorine to 1,2-dichloroethane, the conversion of ethylene with hydrogen chloride with air or oxygen to give 1,2-dichloroethane, the conversion of ethane with hydrogen chloride with air or oxygen to give saturated and unsaturated chlorinated hydrocarbons, preferably 1,2-
25 dichloroethane and vinyl chloride, and the reaction of methane with chlorine.

28 Use of the catalyst pellets according to claims 26-27, wherein the catalyst for the oxychlorination reaction of ethylene contains copper in an amount of 1-12 wt%.

30

29 Use of the catalyst pellets according to claim 28, wherein the catalyst for the oxychlorination reaction of ethylene also comprises at least one of the alkali

metals, alkaline earth metals, group IIB metals and lanthanides in a total amount up to 15 wt%.

30 Use of the catalyst pellets according to claim 29, wherein the alkali metal is
5 lithium, potassium or cesium or a combination of them.

31 Use of the catalyst pellets according to claim 30, wherein the alkali earth
metal is magnesium.

10 32 Use of the catalyst pellets according to claim 31, wherein the lanthanide is
cerium or lanthanum or a combination of them.

33 Use of the catalyst pellets according to claims 26-27, wherein the catalyst
for the oxychlorination reaction of ethane contains copper and/or nickel and an
15 alkali metal.

34 Use of the catalyst pellets according to claim 33, wherein the catalyst for
the oxychlorination reaction of ethane also comprises at least one of the alkaline
earth metals, group IIB metals and lanthanides.

20

35 Use of the catalyst pellets according to claim 34, wherein the catalyst for
the selective oxidation reaction of ethylene comprises at least silver, and at least
one of the alkali and alkaline earth metals.

25 36 Use of the catalyst pellets according to claims 1-24 for selective gas-phase
endothermic reactions.

Abstract**A hollow pellet suitable as carrier of catalysts for selective exothermic reactions**

5 A catalyst hollowed pellet for selective gas phase exothermic reactions in a
tubular fixed bed reactor, having a parallelogram shaped external cross-section.
The catalyst has a low resistance to the flow, allows a good heat exchange with
the wall of the industrial reactor, has a good effectiveness, offers a good
mechanical resistance and guarantee a high total active phase content of the
10 reactor.

In particular with a suitable active phase based on copper and additives
gives a good catalyst for oxychlorination fixed bed processes as well as with a
suitable active phase based on silver and additives gives a good catalyst for
selective oxidation processes.

15

THIS PAGE BLANK (USPTO)

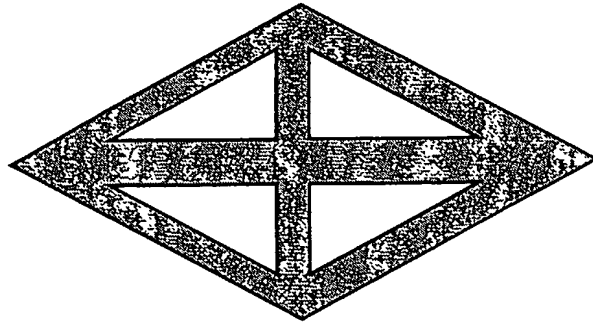
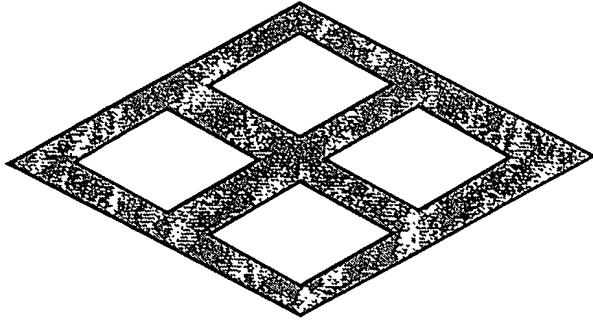
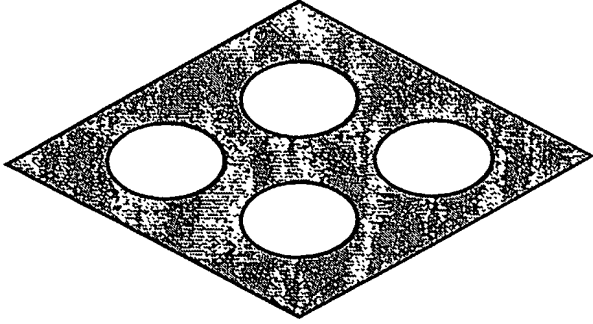


Figure 1

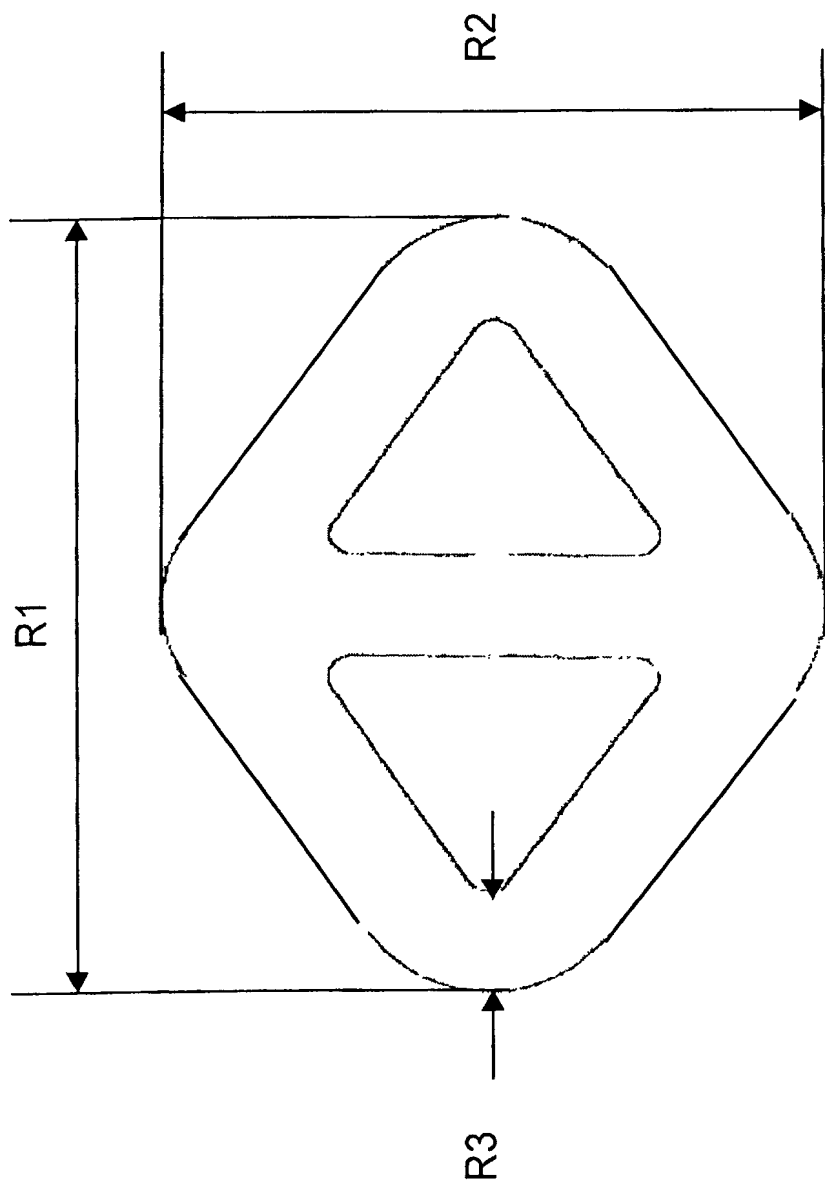


Figure 2

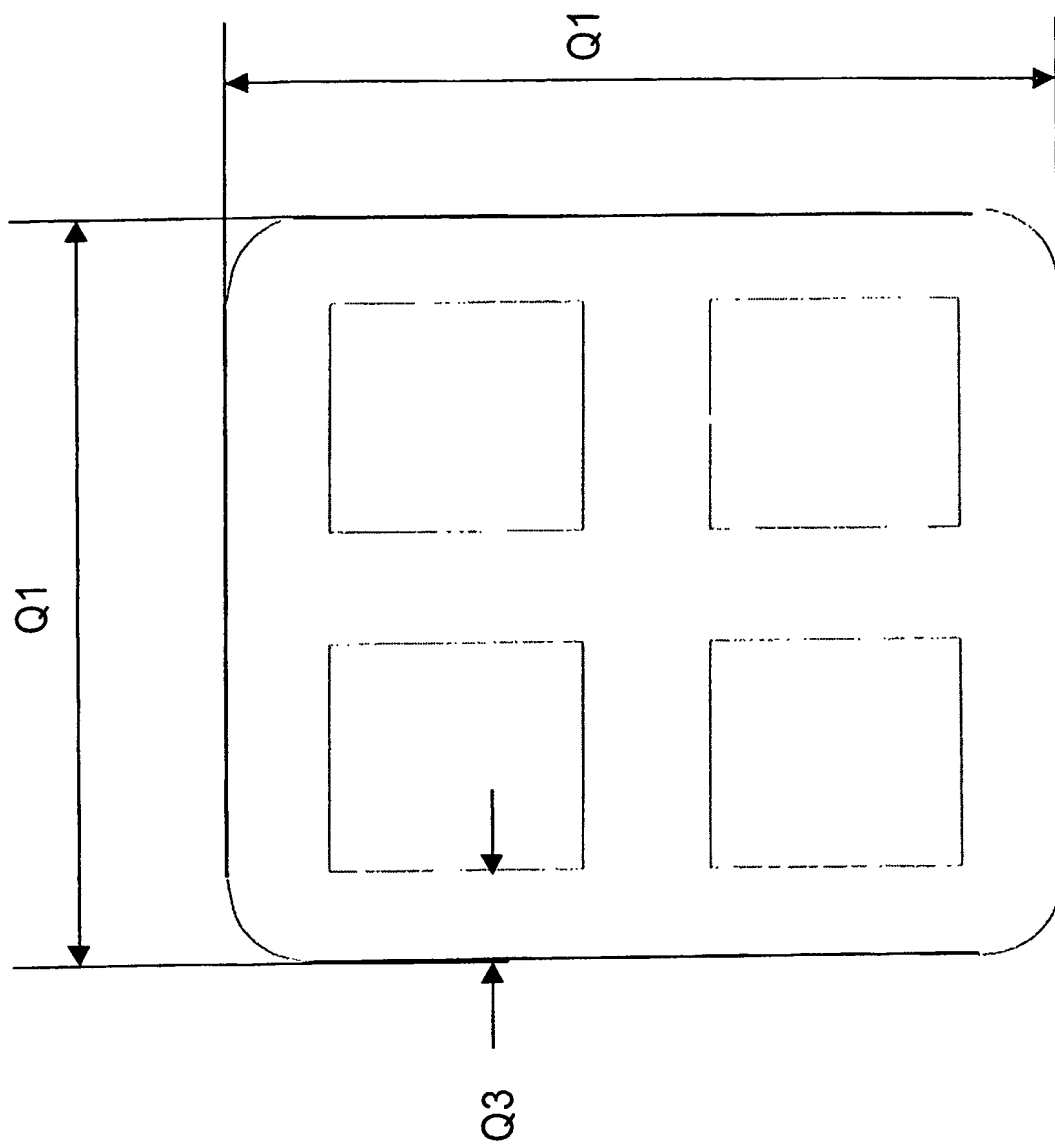


Figure 3

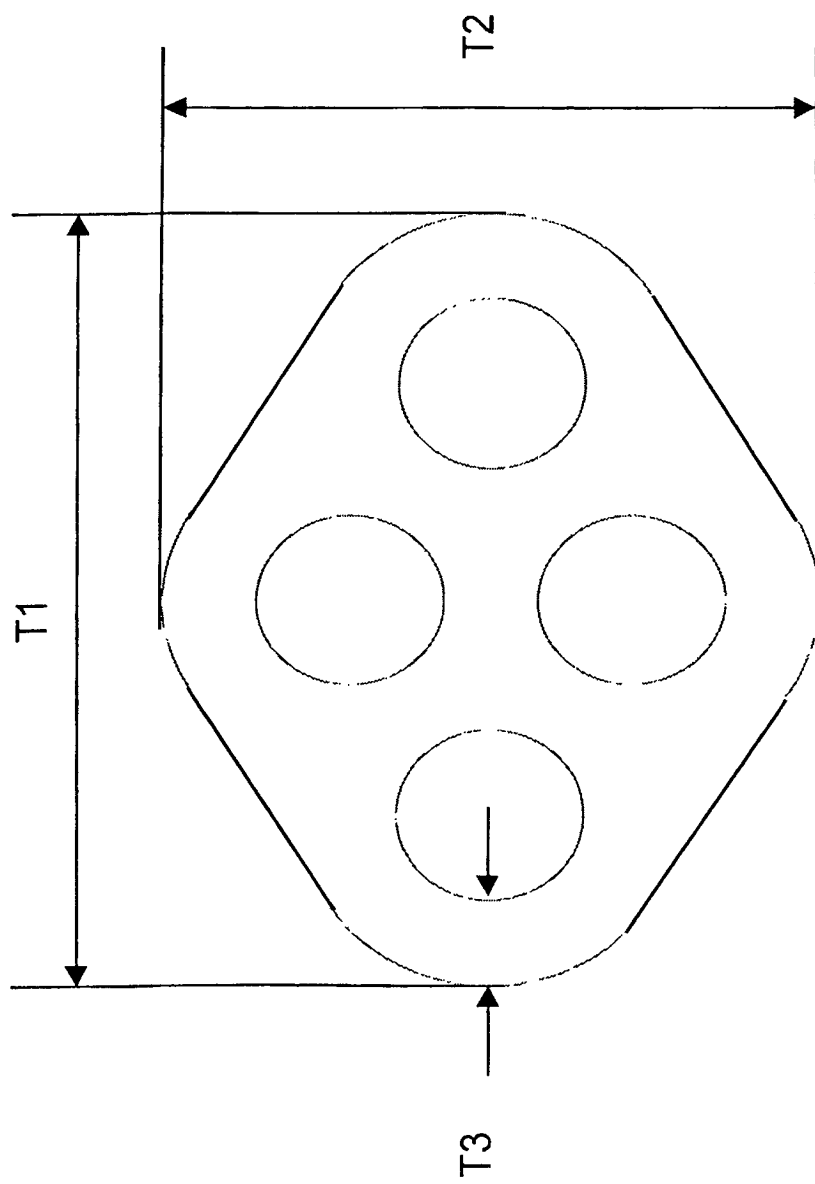


Figure 4

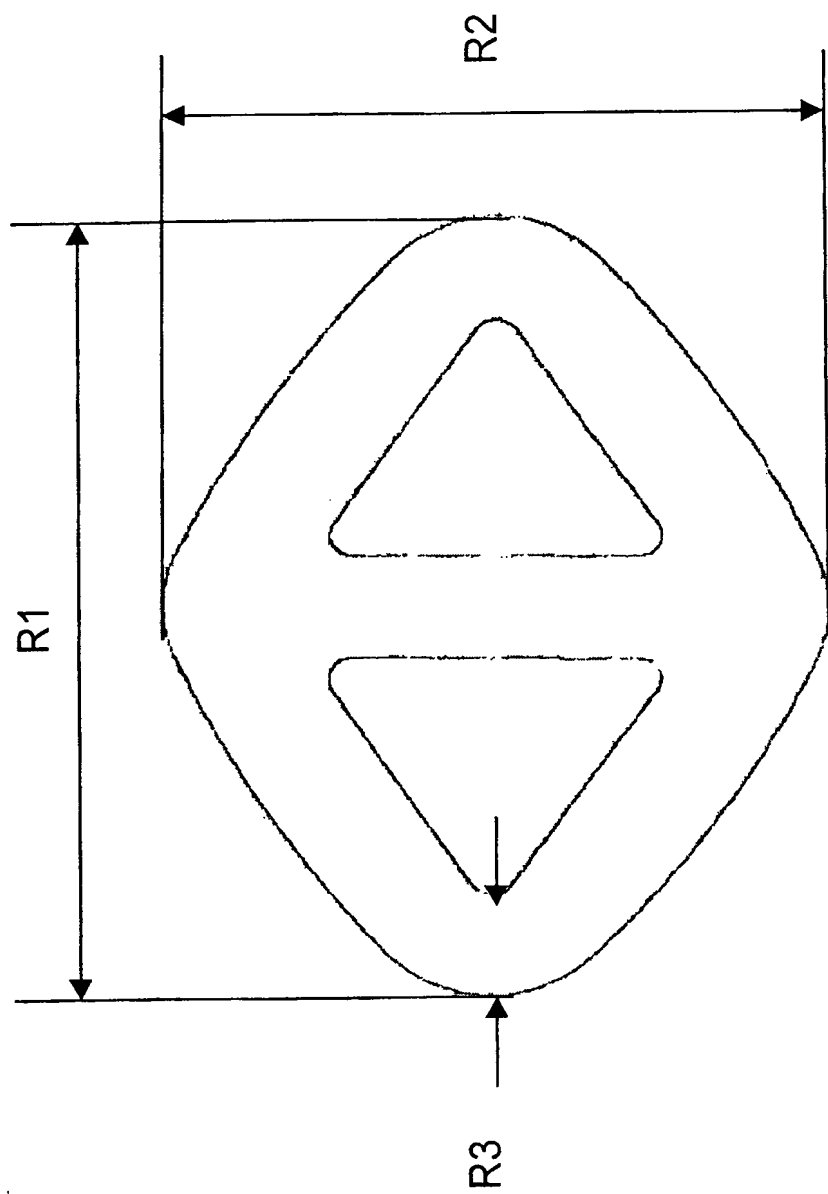


Figure 5

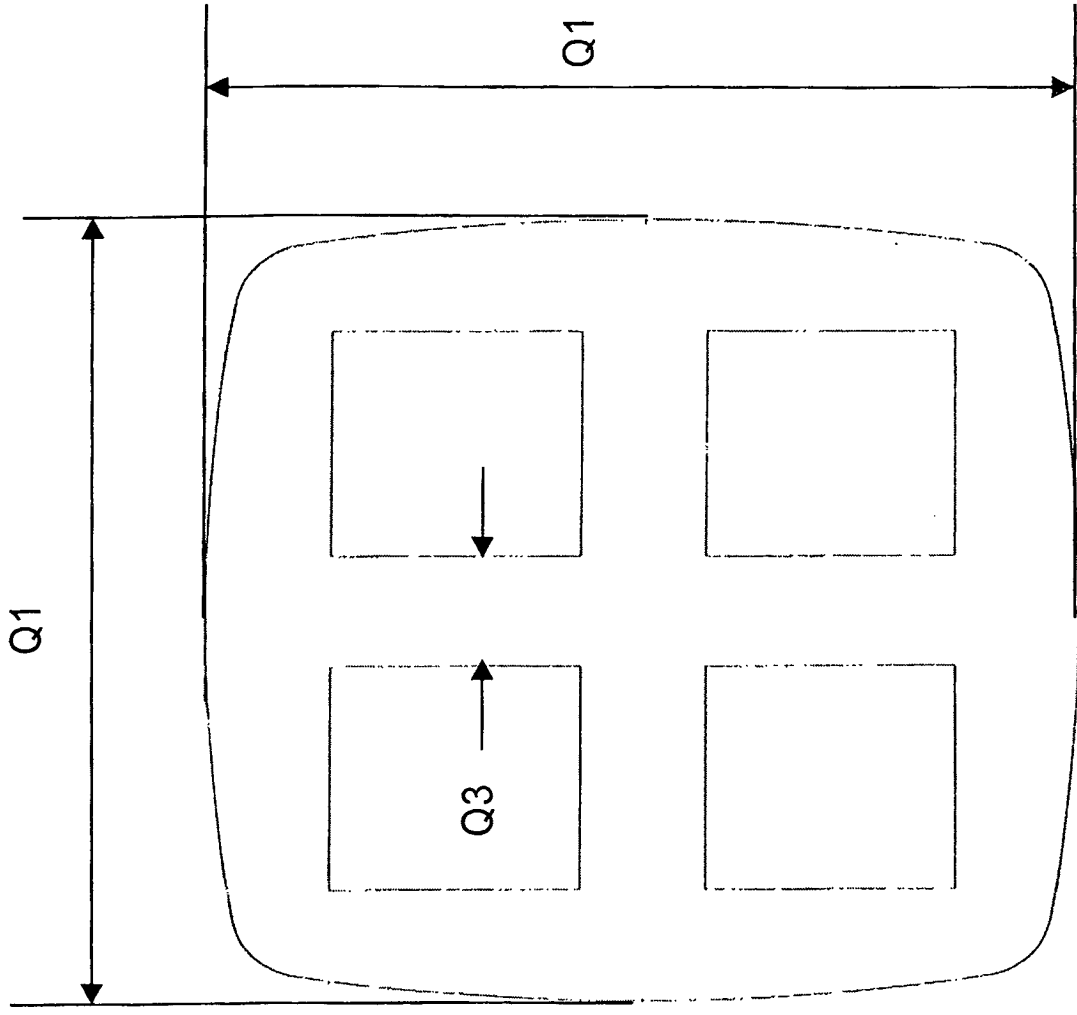


Figure 6

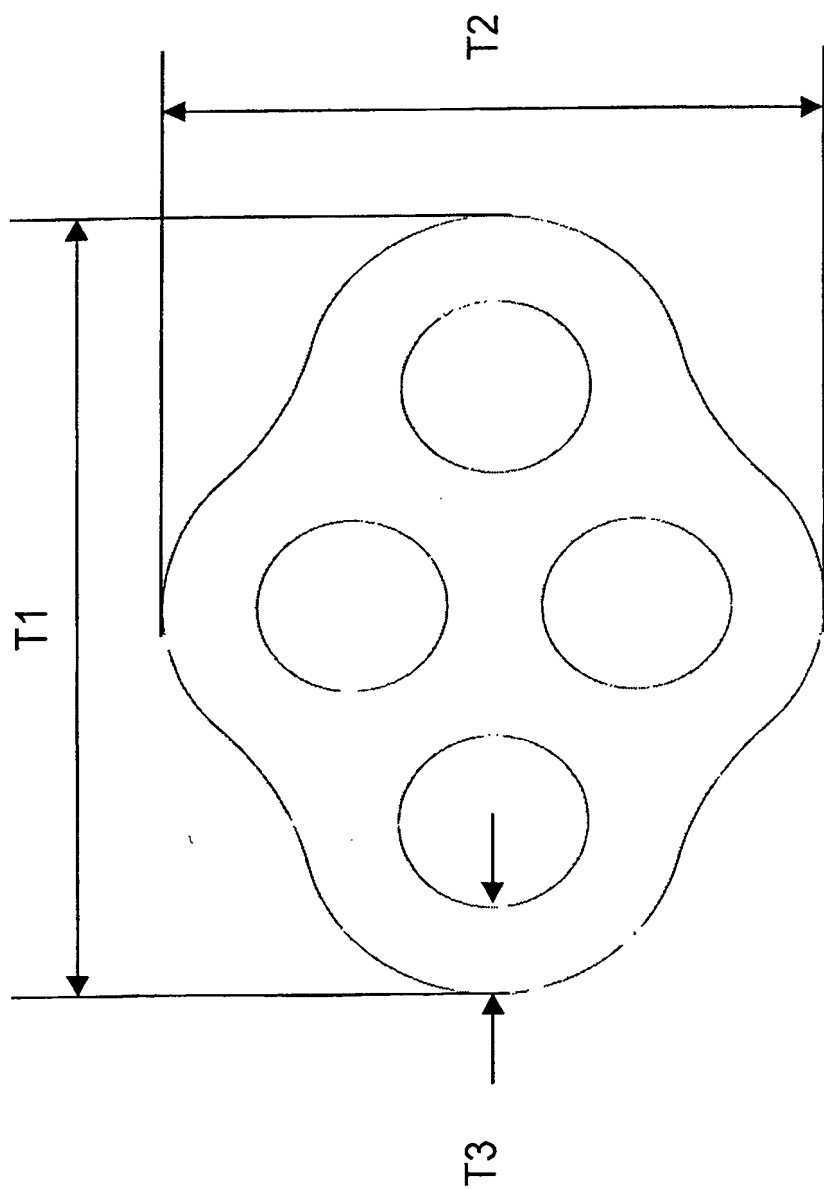


Figure 7

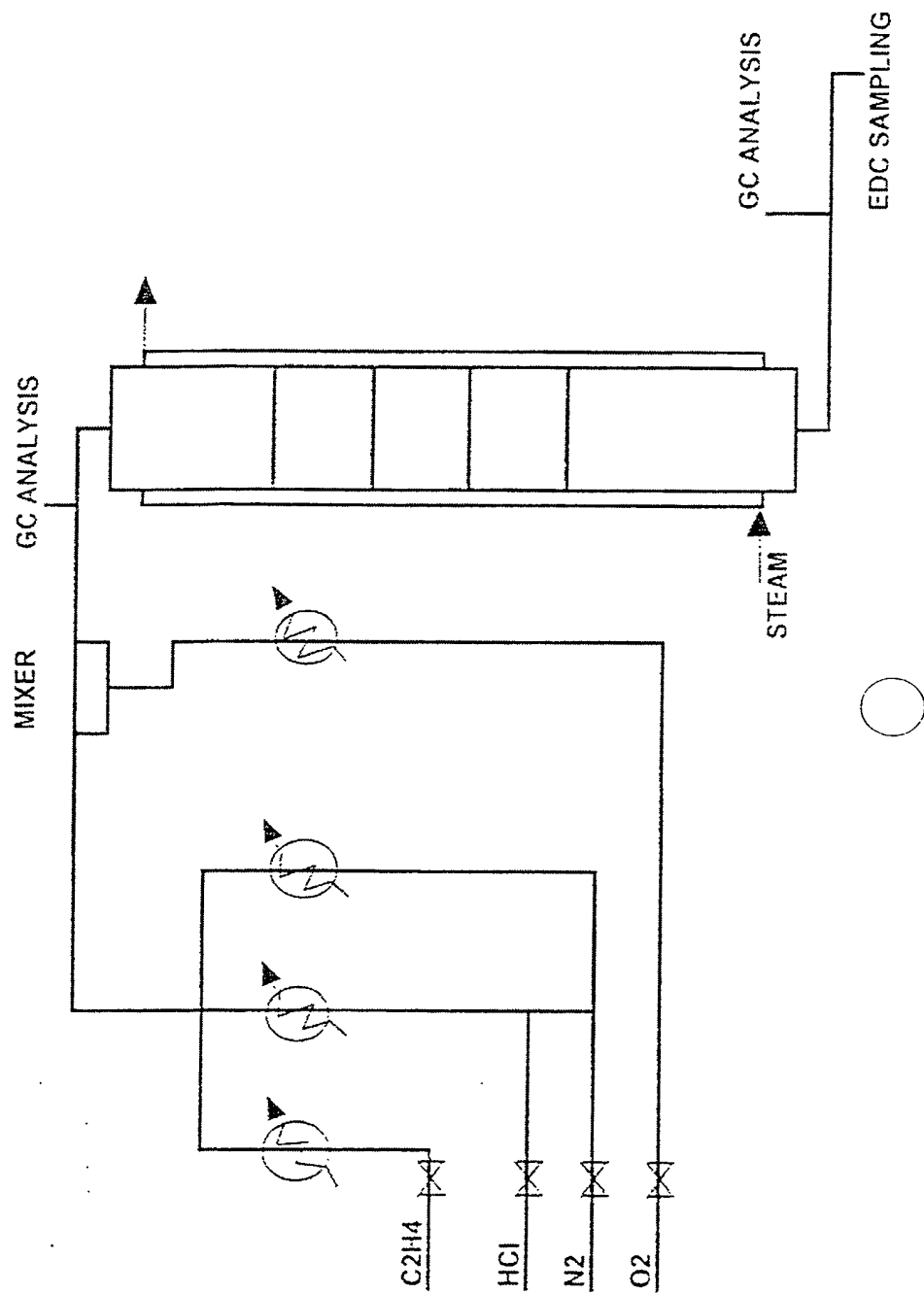


Figure 8